*Galley Proof*

# Soil Chemical Changes Resulting from Irrigation with Water Co-Produced with Coalbed Natural Gas

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## ABSTRACT

Land application of coalbed natural gas (CBNG) co-produced water is a popular management option within northwestern Powder River Basin (PRB) of Wyoming. This study evaluated the impacts of land application of CBNG waters on soil chemical properties at five sites. Soil samples were collected from different depths (0–5, 5–15, 15–30, 30–60, 60–90, and 90–120 cm) from sites that were irrigated with CBNG water for 2 to 3 yr and control sites. Chemical properties of CBNG water used for irrigation on the study sites indicate that electrical conductivity of CBNG water ($EC_w$) and sodium adsorption ratio of CBNG water ($SAR_w$) values were greater than those recommended for irrigation use on the soils at the study sites. Soil chemical analyses indicated that electrical conductivity of soil saturated paste extracts ($EC_s$) and sodium adsorption ratio of soil saturated paste extracts ($SAR_s$) values for irrigated sites were significantly greater ($P < 0.05$) than control plots in the upper 30-cm soil depths. Mass balance calculations suggested that there has been significant buildup of Na in irrigated soils due to CBNG irrigation water as well as Na mobilization within the soil profiles. Results indicate that irrigation with CBNG water significantly impacts certain soil properties, particularly if amendments are not properly utilized. This study provides information for better understanding changes in soil properties due to land application of CBNG water. These changes must be considered in developing possible criteria for preserving fragile PRB ecosystems.

Natural gas is an important source of energy for residential and industrial sectors in the United States. One of our significant sources of natural gas is methane produced from coal seams. Currently, this source of natural gas accounts for approximately 10% of the country's natural gas production and its importance is increasing with time (Pinkser, 2002). Several areas within the United States produce coalbed natural gas (CBNG), of which the Powder River Basin (PRB), covering parts of Wyoming and Montana, is the most active (Wheaton and Olson, 2001). Coalbed natural gas production involves pumping water (hereafter referred to as CBNG water) from coal seams to reduce hydrostatic pressure to facilitate methane release. A single CBNG well can discharge water up to 7.0 $m^3$ $h^{-1}$. Depending on the local conditions and production rates, a CBNG well may be productive for 2 to 20 yr, with an average lifespan of 7 yr. At present there are over 20 000 CBNG wells permitted or drilled in the PRB region and another 50 000 to 100 000 new wells are anticipated in the future. The total CBNG water production in the PRB is expected to peak at about

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47 000 ha-m in 2006 and the cumulative CBNG water production during 2002–2017 is estimated to be 366 000 ha-m (Bureau of Land Management, 2003). Quality of CBNG water is variable within the region and is often not suitable for direct irrigation. The CBNG water in the PRB is dominated by sodium ($Na^+$) and bicarbonate ($HCO_3^-$) ions, with pH ranging from 6.8 to 8.0, $EC_w$ from 0.4 to 4 dS $m^{-1}$, $SAR_w$ from a low of 5 to a high of 70 $mmol^{1/2}$ $L^{-1/2}$, and total dissolved solids concentrations from 270 to 2720 mg $L^{-1}$ (Rice et al., 2002; Van Voast, 2003).

Clearly, management of this enormous quantity of CBNG water produced in the PRB presents a major environmental challenge. Management of these waters is influenced by economics, regulatory guidelines, and environmental impacts. Water issues surrounding CBNG are contentious (King et al., 2004). Use and disposal of CBNG waters is a primary environmental concern of the public, leading to many legal and regulatory battles in Wyoming and other CBNG regions (Bureau of Land Management, 2003; Vance et al., 2004, p. 31–34).

At present different CBNG water management approaches used in Wyoming include injection, direct discharge to surface waters, treatment and release of CBNG water into streams, impoundments, infiltration reservoirs, and land application (Bureau of Land Management, 2003). Unlike other CBNG-producing regions in the United States, injection is problematic in PRB (except in the Pinedale region of Wyoming) because of complications arising from managing multiple producing zones and multiple producers (Bureau of Land Management, 2003). Therefore, very little injection is practiced in the PRB, except in replenishing the city of Gillette's water supply (Vance et al., 2004, p. 31–34). Wyoming has allowed some CBNG producers in the PRB to release limited amounts of CBNG water directly into waterways (King et al., 2004). Some CBNG producers are treating poor-quality CBNG water using ion exchange, reverse osmosis, and other similar types of treatments to improve quality for release into streams and other waterways, or for beneficial purposes such as irrigation use. Unfortunately, the different types of CBNG-water treatment often require large industrial columns and filters, specialized equipment, and operation and maintenance efforts that are very expensive (Vance et al., 2004, p. 31–34). However, at present there is a moratorium on additional direct-discharge permits, in part, because impacts to downstream users have not been completely evaluated.

Coalbed natural gas water has also been discharged

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EXHIBIT 8

into lined or unlined impoundments (e.g., reservoirs). Storage in lined impoundments allows CBNG waters to be treated for land application for agricultural purposes or disposal, and provides enhanced control over the timing of discharges into surface water bodies during non-irrigation seasons. Unlined impoundments allow water to leach into the subsurface environment or percolate into the surrounding soil. Lateral migration of salts and $Na^+$ that may impact surrounding streams and terrestrial ecosystems are a possible consequence of long-term CBNG-water disposal in unlined impoundments (Bureau of Land Management, 2003).

Use of CBNG water for irrigation of grazing lands and agricultural production is gaining popularity in Wyoming (Ganjegunte et al., 2004). Smectites dominate PRB soil clay minerals and nearly 41% of the PRB area is covered with soils characterized by poor drainage (Bureau of Land Management, 2003). Application of poor quality CBNG water on these lands can have serious negative impacts on certain soil properties (Rice et al., 2002; Dahiya et al., 2004). To avoid permanent damage to fragile PRB ecosystems, a better understanding of potential impacts to lands receiving CBNG water is essential. The main purpose of this study was to assess changes in soil properties due to CBNG-water irrigation. A field study was conducted to (i) evaluate the quality of CBNG water being used for irrigation in the PRB region that is actively producing CBNG waters and (ii) examine changes in soil chemical properties due to land application of CBNG waters.

## MATERIALS AND METHODS

### Study Area

The PRB, located in northeast Wyoming and southeast Montana (Fig. 1), is situated between the Black Hills to the east, the Big Horn Mountains to the west, and the Miles City Arch to the north. The land surface generally slopes northward from higher elevations in Wyoming and drains to the Yellowstone River in Montana. The Tongue River Member of the Fort Union Formation contains coal that is mined in both Wyoming and Montana and is the source unit for CBNG. Ground water flow in the PRB is also generally from the south to the north. Coal seams are often continuous water-bearing units that provide an important ground water source; shallow coal seams are readily tapped as water resources for livestock (Wheaton and Olson, 2001). Soils of the PRB have developed under a climatic regime characterized by cold winters, warm summers, and low to moderate precipitation (e.g., rainfall of 300 to 380 mm including snowfall of 910 to 1520 mm). Soil textures vary and are influenced by dominant geologic conditions. Soils are generally alkaline and low in organic matter. Farming occurs primarily along valleys with perennial streams that support irrigation (Bureau of Land Management, 2003).

### Study Sites, Water, and Soil Sampling

Five sites that have received CBNG water irrigation over a period of 2 to 3 yr (irrigation seasons) were selected to evaluate impacts on soil chemical properties. These sites are located in Johnson and Sheridan counties in Wyoming (Fig. 1). Different CBNG producers have been managing these sites, and irrigation with CBNG water is performed from April to November. Various water treatments and soil amendments are being used.

Ownership and access issues limited possible study site location. Control sites were selected that were in close proximity to the irrigated sites; all control sites did not receive CBNG water irrigation. Soil map units, soil series composition, and size of irrigated and control sites are listed in Table 1. Soil samples used for physical and chemical analyses for this study were somewhat variable relative to textures of soil series of the different mapping units. Various water and soil amendments being used in these study sites are summarized in Table 2. The data on the amount of CBNG water, gypsum, and elemental S (as per management records of CBNG producers managing these sites) that have been added to irrigated soils are given in Table 3. The amount of S added as soil amendments (Table 3) does not include S supplied by the sulfur burners.

Coalbed natural gas waters from multiple wells (10–20) are discharged into holding ponds to be used for irrigation at a later date. Triplicate samples from the ponds used for irrigating the study sites were collected in plastic bottles during June–July 2003 and October–November 2003. Sites 2 and 5 received CBNG water from the same source. Samples were transported to the laboratory and analyzed for pH, $EC_w$, Na, Ca, and Mg concentrations within 24 to 48 h after collection using the methods described below.

A soil auger was used to randomly collect five replicate soil samples from six depths (0–5, 5–15, 15–30, 30–60, 60–90, and 90–120 cm) from each of the irrigated and control sites during the beginning (May–June) and three replicate soil samples at the end (October–November 2003) of the irrigation season. The entire irrigated area was available for sampling to ensure that samples were representative of irrigated sites. Because gas companies maximize the area available for disposal of CBNG water, control areas were limited to areas much smaller than irrigated sites. Samples were stored in resealable plastic bags to prevent moisture loss during transportation to the laboratory. Subsamples were dried at 105°C until constant weight was obtained, and soil moisture contents were determined using the difference between field-moist and oven-dry weights. The depth at which soil moisture content was the greatest was assumed to be the wetting depth at the time of sampling. Soil samples were air-dried, passed through a 2-mm sieve, and analyzed for particle-size distribution and chemical properties. Soil texture was determined using the hydrometer method (Gee and Bauder, 1986).

### Chemical Analyses

The pH and EC values for CBNG water samples and soil saturated paste extracts were determined using pH and EC electrodes (meters), respectively (Rhoades. 1999; Thomas, 1999). Soluble Na, Ca, and Mg concentrations in soil saturated paste extracts and CBNG water samples were determined using inductively coupled plasma spectrometry (Suarez, 1999).

The SAR of CBNG waters and saturated paste extracts was calculated as:

$$SAR \ (mmol^{1/2} \ L^{-1/2}) = [Na^+]/[Ca^{2+} + Mg^{2+}]^{1/2} \quad [1]$$

where Na, Ca, and Mg represent millimolar concentrations ($mmol \ L^{-1}$) of the respective ions.

Soil cation exchange capacity (CEC) was determined by using sodium acetate (NaOAc) buffered at pH 8.2 (Chapman, 1965). Briefly, a 5-g soil sample was washed three times with 33 mL of 1 $M$ NaOAc to saturate the exchange complex with $Na^+$. After removing the excess $Na^+$ with one ethanol wash, the soil was washed with three volumes of 1 $M$ ammonium acetate ($NH_4OAc$ buffered at pH 7) to displace $Na^+$ from the exchange complex. The contents were centrifuged for 10 min at 670 × $g$. The three supernatants were combined in a 100-mL volumetric flask, brought to volume with 1 $M$ $NH_4OAc$, and
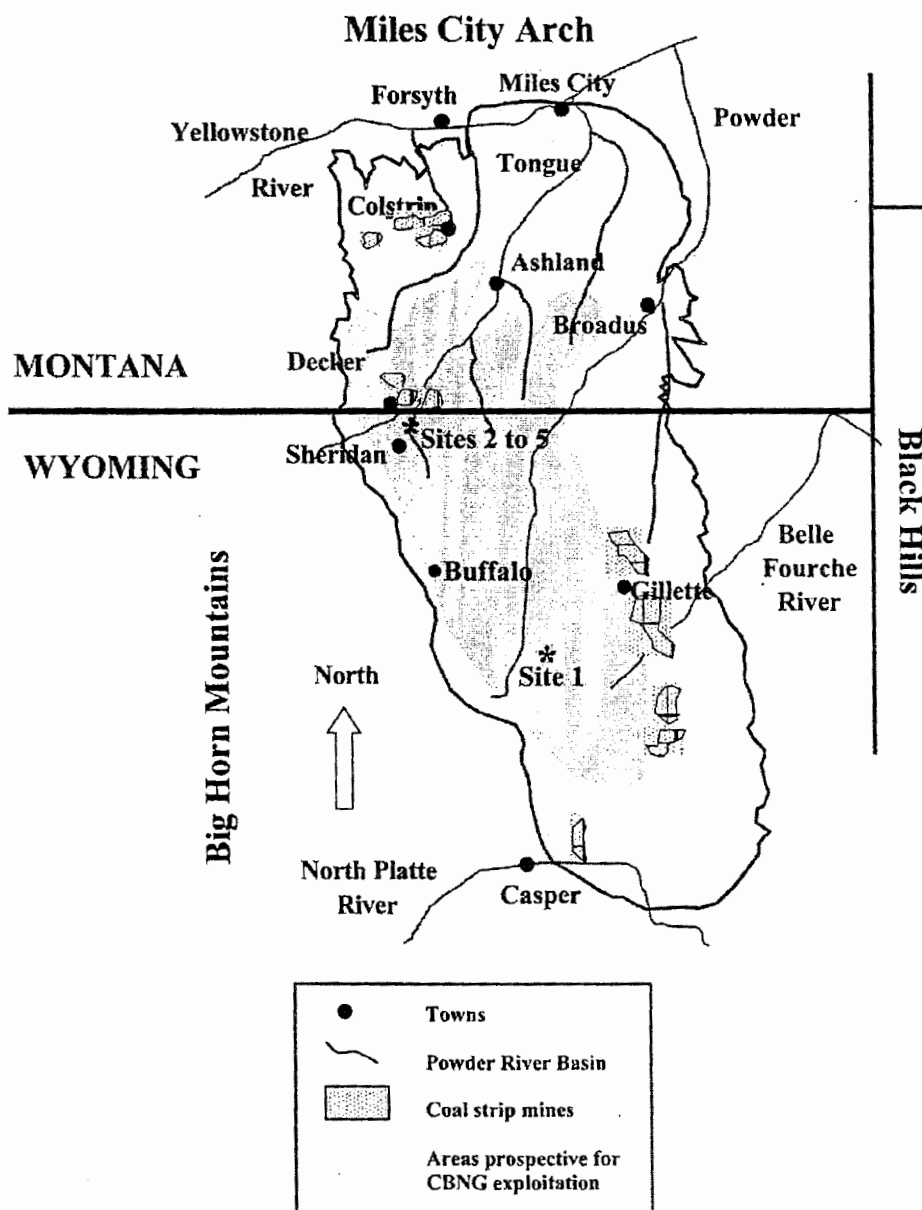
**Miles City Arch**

Fig. 1. Extensive coal reserves in the Powder River Basin (PRB) cover parts of Wyoming and Montana. The PRB region in Wyoming is currently the most active coalbed natural gas (CBNG)-producing area in the United States.

analyzed for Na$^+$ using atomic absorption spectrophotometry. Concentrations of Na$^+$ in the final solutions were used to calculate soil CEC.

## Mass Balance for Sodium

Soil Na concentrations were evaluated using mass balance calculations. The amount of Na added through CBNG water for each site was calculated using both Na concentration and volume of CBNG water added over time. Ammonium acetate (NH$_4$OAc) extractable Na in irrigated and control soil samples represented the sum of soil water-soluble and exchangeable Na. Soil water-soluble Na concentrations were determined using Na concentrations in soil saturated paste extracts and the mois-

ture content at saturation (United States Salinity Laboratory Staff, 1954). Water-soluble Na concentrations were subtracted from Na contents in the NH$_4$OAc extracts to determine exchangeable Na concentrations (Helmke and Sparks, 1996). Bulk densities of soil samples at different depths in irrigated and control sites were determined by using the core method described by Grossman and Reinsch (2002). The mean bulk density values ranged from 1.01 Mg m$^{-3}$ at a 0- to 5-cm depth in Site 2 control to 1.71 Mg m$^{-3}$ at a 15- to 30-cm depth in Site 6 (data not presented). Soil water-soluble and exchangeable Na concentrations, soil depth, and bulk density values were used to calculate the Na content present in soils at different depths to 120 cm for each site. Differences between the sums of soil water-soluble and exchangeable Na in the irri-

Table 1. Soil map units, soil series composition, and area details for study sites.†

| Site | Irrigated Classification By soil map unit | Irrigated Classification By soil series | Area | Control Classification By soil map unit | Control Classification By soil series | Area |
|---|---|---|---|---|---|---|
| | | | ha | | | ha |
| 1 | not indicated (map for north Johnson county not available) | Zigweid (fine-loamy, mixed, superactive, mesic Ustic Haplocambid) | 17 | not indicated (map for north Johnson county not available) | Zigweid | 1 |
| 2 | Shingle–Worf complex | Shingle (loamy, mixed, superactive, calcareous, mesic, shallow Ustic Torriorthent); Worf (loamy, mixed, superactive, mesic, shallow Ustic Haplargid) | 17 | Cushman–Worf association | Cushman (fine-loamy, mixed, superactive, mesic Ustic Haplargid); Worf | 2 |
| 3 | Bidman-moist-Ulm loam and Parmleed–Bidman association | Bidman (fine, smectitic, mesic Ustic Paleargid); Ulm (fine, smectitic, mesic Ustic Haplargid); Parmleed (fine, smectitic, mesic Ustic Paleargid) | 12 | Parmleed–Worfka and Parmleed–Bidman associations | Parmleed; Worfka; Bidman | 1 |
| 4 | Wyarno clay loam | Wyarno (fine, smectitic, mesic Ustic Haplargid) | 8 | Wyarno clay loam | Wyarno | 1 |
| 5 | Parmleed–Worfka association | Parmleed; Worfka (clayey, smectitic, mesic, shallow Ustic Haplargid) | 2 | Parmleed–Worfka and Parmleed–Bidman associations | Parmleed; Worfka; Bidman | 1 |

† Soil map unit classifications are based on NRCS soil surveys for Sheridan and Johnson Counties with field verifications by NRCS, Bureau of Land Management, and private consulting soil scientists.

Table 2. Details of water application methods, water treatments, soil treatments, and years of water application in the study sites managed by different coalbed natural gas (CBNG) producers.

| Site | County | Water treatment before irrigation | Soil treatment and/or amendments | Years of irrigation |
|---|---|---|---|---|
| 1 | Johnson | none | surface application of gypsum and elemental S | 3 |
| 2 | Sheridan | sulfur burner | surface application of gypsum and elemental S | 3 |
| 3 | Sheridan | sulfur burner | surface application of gypsum and elemental S | 2 |
| 4 | Sheridan | sulfur burner | surface application of gypsum and elemental S | 2 |
| 5 | Sheridan | sulfur burner | surface application of gypsum and elemental S | 3 |

Table 3. Details of coalbed natural gas (CBNG) water and soil chemical amendments added to irrigated sites managed by different CBNG producers.†

| | 2001 (September–November) | 2002 (April–November) | 2003 (April–November) |
|---|---|---|---|
| | | Site 1 | |
| Water, ha-m | 0.22 | 0.55 | 0.55 |
| Sulfur, Mg ha$^{-1}$ | 3.08 | 9.38 | 16.3 |
| Gypsum, Mg ha$^{-1}$ | 8.03 | 13.3 | 21.3 |
| | | Site 2 | |
| Water, ha-m | 0.30 | 0.30 | 0.30 |
| Sulfur, Mg ha$^{-1}$ | 2.50 | 2.50 | 2.50 |
| Gypsum, Mg ha$^{-1}$ | 4.25 | 4.25 | 4.25 |
| | | Site 3 | |
| Water, ha-m | | 0.30 | 0.30 |
| Sulfur, Mg ha$^{-1}$ | | 2.50 | 2.50 |
| Gypsum, Mg ha$^{-1}$ | | 4.25 | 4.25 |
| | | Site 4 | |
| Water, ha-m | | 0.30 | 0.30 |
| Sulfur, Mg ha$^{-1}$ | | 2.50 | 2.50 |
| Gypsum, Mg ha$^{-1}$ | | 4.25 | 4.25 |
| | | Site 5 | |
| Water, ha-m | 0.30 | 0.30 | 0.30 |
| Sulfur, Mg ha$^{-1}$ | 2.50 | 2.50 | 2.50 |
| Gypsum, Mg ha$^{-1}$ | 4.25 | 4.25 | 4.25 |

† The above data are obtained from management records of CBNG producers maintaining the study sites and based on our mass balance calculations these data were found to be fairly accurate.

gated and versus control sites represent Na that was added through CBNG water and/or mobilized in soil profiles through dissociation of Na salts.

## Statistical Analysis

Differences in CBNG water chemistry were evaluated using a one-way ANOVA. Differences between irrigated and control sites for different parameters were evaluated by carrying out two-sample $t$ tests that assumed equal variances for the parameters. All tests for significance were performed at $P < 0.05$, unless otherwise noted.

## RESULTS AND DISCUSSION

### Coalbed Natural Gas Water Chemistry

The CBNG water pH values ranged from 7.7 to 8.2, $EC_w$ from 2.0 to 2.9 dS m$^{-1}$, and SAR$_w$ from 17.2 to 32.8 mmol$^{1/2}$ L$^{-1/2}$ (Table 4). There were no significant differences in pH, EC, Ca, and Mg concentrations among the CBNG waters collected from the different sites. The CBNG water from Site 4 had a significantly lower SAR$_w$ value than CBNG waters collected from Sites 1 and 3. Further, Na concentrations in CBNG waters of Site 1 were significantly greater than those of Sites 2, 3, 4, and 5. Chemistry of the late-season CBNG water samples did not differ significantly from their respective early-

**Table 4. Selected chemical properties of coalbed natural gas (CBNG) water samples.**

| pH | EC | SAR | | Ca | Mg | Na |
|---|---|---|---|---|---|---|
| | dS m$^{-1}$ | mmol$^{1/2}$ L$^{-1/2}$ | | | mg L$^{-1}$ | |
| | | | Site 1 | | | |
| 8.2 ± 0.1 | 2.9 ± 0.9 | 30.9 ± 2.1a† | | 12.8 ± 7.1 | 30.0 ± 0.3 | 888 ± 7.80a |
| | | | Site 2 | | | |
| 8.0 ± 0.5 | 2.0 ± 0.4 | 24.2 ± 4.9ab | | 11.8 ± 3.4 | 7.0 ± 1.1 | 392 ± 68.6b |
| | | | Site 3 | | | |
| 7.9 ± 0.9 | 2.2 ± 0.3 | 32.8 ± 5.9a | | 9.9 ± 6.7 | 4.7 ± 0.5 | 485 ± 19.5b |
| | | | Site 4 | | | |
| 7.7 ± 0.3 | 2.9 ± 1.2 | 17.2 ± 2.2b | | 11.9 ± 2.9 | 16.4 ± 5.0 | 378 ± 5.10b |
| | | | Site 5 | | | |
| 8.0 ± 0.5 | 2.0 ± 0.4 | 24.2 ± 4.9ab | | 11.8 ± 3.4 | 7.0 ± 1.1 | 392 ± 68.6b |

† Means followed by the same lowercase letter are not significantly different from other values in that column at the 0.05 probability level.

season samples, which would be expected if the same source water were used. The $EC_w$ and $SAR_w$ values determined in our study are in agreement with those reported in the Bureau of Land Management environmental impact statement (Bureau of Land Management, 2003) for Johnson and Sheridan counties. Our results are on the high side of the range reported by Rice et al. (2002) and greater than the values reported by McBeth et al. (2003) for CBNG water samples from various PRB locations. Sodium enrichment in CBNG waters collected in the present study is attributed to ion exchange during ground water flow in the northwest PRB of Wyoming. The CBNG water chemistry is influenced by (i) dissolution of plagioclase feldspars, (ii) exchange of Ca and Mg for Na on clay complexes or removal of Ca or Mg by carbonate or sulfate precipitation, and (iii) bacterially mediated processes associated with coal formation (Shainberg et al., 1989; Law and Rice, 1993; Wheaton and Olson, 2001; Rice et al., 2002). The net effects of these processes are natural gas production, with increased $Na^+$ and $HCO_3^-$ concentrations and decreased $SO_4^{2-}$ concentrations in associated waters.

Based on United States Salinity Laboratory Staff (1954) irrigation water classification, early-season CBNG waters of Sites 1, 2, 3, 4, and 5 were classified as C4S4, C3S3, C3S4, C4S3, and C3S3, respectively. The late-season samples from these sites were classified the same as the early-season samples, except for Sites 3 (C4S4) and 4 (C3S3). The key irrigation water-quality parameters are $EC_w$ and $SAR_w$. Based on $EC_w$, CBNG waters are classified in the medium salinity class that indicates potential detrimental effects on sensitive crops and the need for careful water management (Ayers and Westcot, 1985). The term $SAR_w$ describes the sodicity hazard of irrigation water. The sodium hazard associated with irrigation water is dependent not only on $SAR_w$ but also on $EC_w$ and the dominant clay minerals present in soil. The dominant clay minerals present in study site soils are smectites (Bureau of Land Management, 2003), and the $EC_w$ of CBNG waters ranged from 2.0 to 2.9. Based on this information, a moderate potential sodium hazard ($SAR_w$ range of 17 to 33) is associated with the CBNG water, if used for irrigation (Ayers and Westcot, 1985). Another important factor that increases the sodium hazard of irrigation waters is alkalinity ($HCO_3^- + CO_3^{2-}$). Although total alkalinity of the samples was not determined in the present study, previous studies have indicated that CBNG waters have high alkalinity concentrations (Rice et al., 2002; McBeth et al., 2003; Bureau of Land Management, 2003; Van Voast, 2003). In soil solutions $Ca^{2+}$ readily reacts with the carbonate species to form calcite ($CaCO_3$), which removes $Ca^{2+}$ ions from solution, favoring their replacement by $Na^+$ on the soil exchange complex (Essington, 2003; McBeth et al., 2003).

## Soil Chemical Properties

Soil pH values at irrigated sites were significantly greater than those of control sites at Site 1 (0–5 cm), Site 2 (90–120 cm), and Site 5 (30–60 cm) (Fig. 2). Saturated paste extract $EC_e$ values for samples from irrigated sites (Fig. 3) were significantly greater than those from their respective control sites in the upper 30-cm depth. For the 30- to 60-cm depth, irrigated soil $EC_e$ was significantly greater than control soils at Sites 1, 3, and 4. Site 2 irrigated soils had significantly lower $EC_e$ values than that of control at a depth of 90 to 120 cm. In general, irrigated site $EC_e$ values decreased with depth in the upper 60 cm. The CECs of soils in irrigated and control Sites 1, 2, 3, 4, and 5 ranged from 12 to 32, 5 to 26, 5 to 31, 8 to 32, and 8 to 37 cmol$_{(-)}$ kg$^{-1}$, respectively (data not presented). No significant differences were observed between CEC values of irrigated and control sites, except for the 15- to 30- and 60- to 120-cm depths at Site 3.

In arid environments, use of ground waters with appreciable salt concentrations ($EC_w > 0.75$ dS m$^{-1}$) for irrigation on soils with poor drainage can result in salt buildup due to solubilization of soil salts that do not leach below the root zone (Manchanda, 1995; Tedeschi and Menenti, 2002). Irrigating with shallow aquifer ground waters containing greater salt concentrations ($EC_w > 0.75$ dS m$^{-1}$), such as CBNG water, can contribute to elevated soil $EC_e$ values (Chhabra, 1996). Dissolution of soil salts and contribution of salts from CBNG water irrigation coupled with poor drainage of PRB soils (Bureau of Land Management, 2003) and high evapotranspiration rates have the potential for increasing soluble salts in the root zone (the active root zone at these sites is 60 cm, according to local personnel of the Natural Resources Conservation Service) (Gallagher, 1986; Burrow et al., 2002). Based on CBNG $EC_w$ and $EC_e$ of soil solutions,
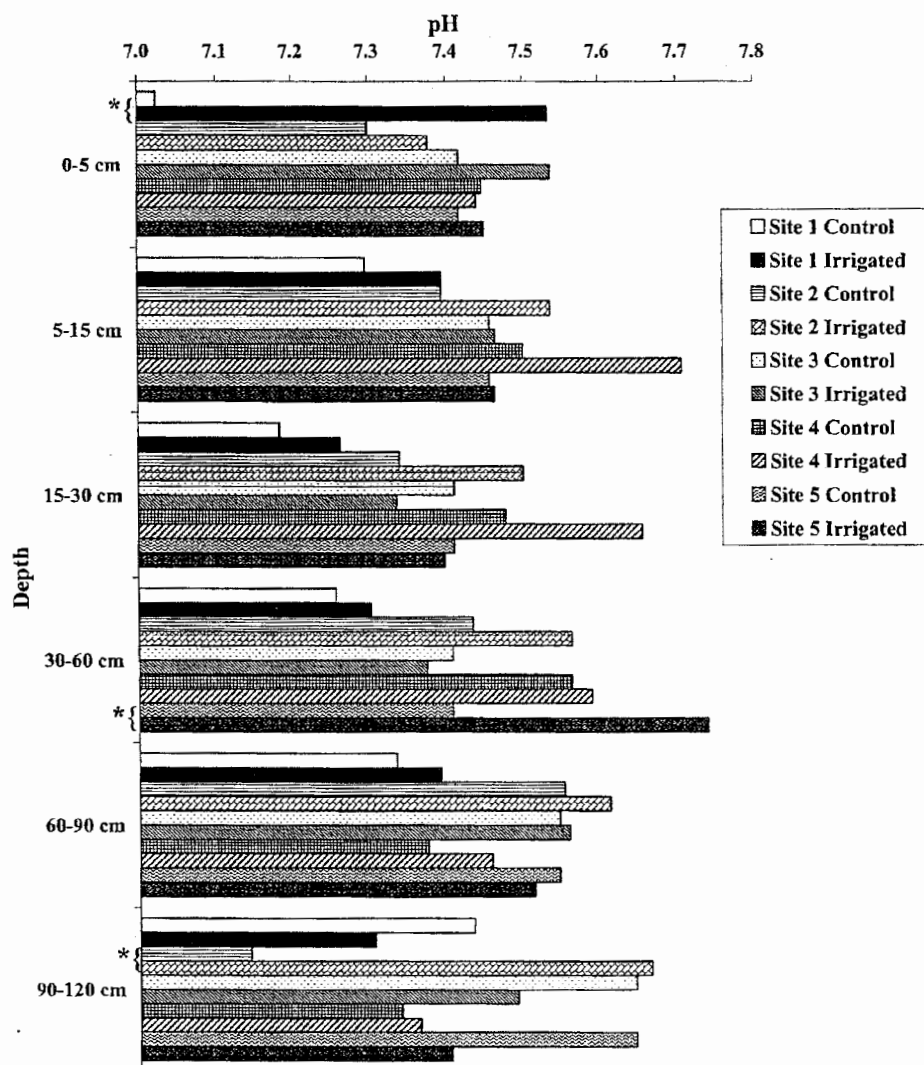
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Fig. 2. Mean soil solution pH values of samples from control and irrigated sites. Significant differences between irrigated and control samples at the 0.05 probability level are noted with asterisks.

it may be inferred that the salinity levels in the irrigated site soils are greater than threshold values for sensitive to moderately sensitive crops (Mass, 1990).

Soil solution $SAR_e$ values of CBNG irrigated sites were significantly greater than those of control sites to a depth of 30 cm, except at Site 2 (Fig. 4). The $SAR_e$ values of irrigated soils in Sites 1 and 4 were significantly greater than those of control sites at depths of 30 to 60 cm. Site 2 $SAR_e$ values of the irrigated and control soils were not significantly different perhaps due, in part, to higher sand contents at the irrigated sites (Endo et al., 2002).

Soils with $EC_e > 4$ dS m$^{-1}$ and $SAR_w < 13$ mmol$^{1/2}$ L$^{-1/2}$ are considered saline, whereas soils with $EC_e > 4$ dS m$^{-1}$ and $SAR_e > 13$ mmol$^{1/2}$ L$^{-1/2}$ are considered saline-sodic soils (United States Salinity Laboratory Staff, 1954; Gupta and Abrol, 1990; Chhabra, 2005). Irrigated soils at a depth of 0 to 15 cm in Site 1 and a

depth of 0 to 5 cm in Site 4 are classified as saline-sodic. Soils at depths of 15 to 60 cm at Site 1 and 0 to 5 cm at Site 3 are saline, whereas soils at Sites 2, 4, and 5 are potentially saline. For other sites, soil $EC_e$ and $SAR_e$ values were less than the critical limits. However, trends of increasing sodicity with extended periods of irrigation with CBNG water were apparent. Soil samples were collected during the beginning and end of the irrigation season, with depth at maximum moisture content occurring at 30 to 60 cm in irrigated site samples. Accordingly, 30 to 60 cm was assumed to be the characteristic depth of wetting in these soils, which suggested that changes in soil chemistry in the upper 60-cm depths could be attributable to CBNG water irrigation.

Increase in $SAR_e$ values is partially due to the accumulation of Na in irrigated soils due to dissolution and mobilization of Na salts in soils apart from addition of Na through CBNG water (Table 5). Although concen-
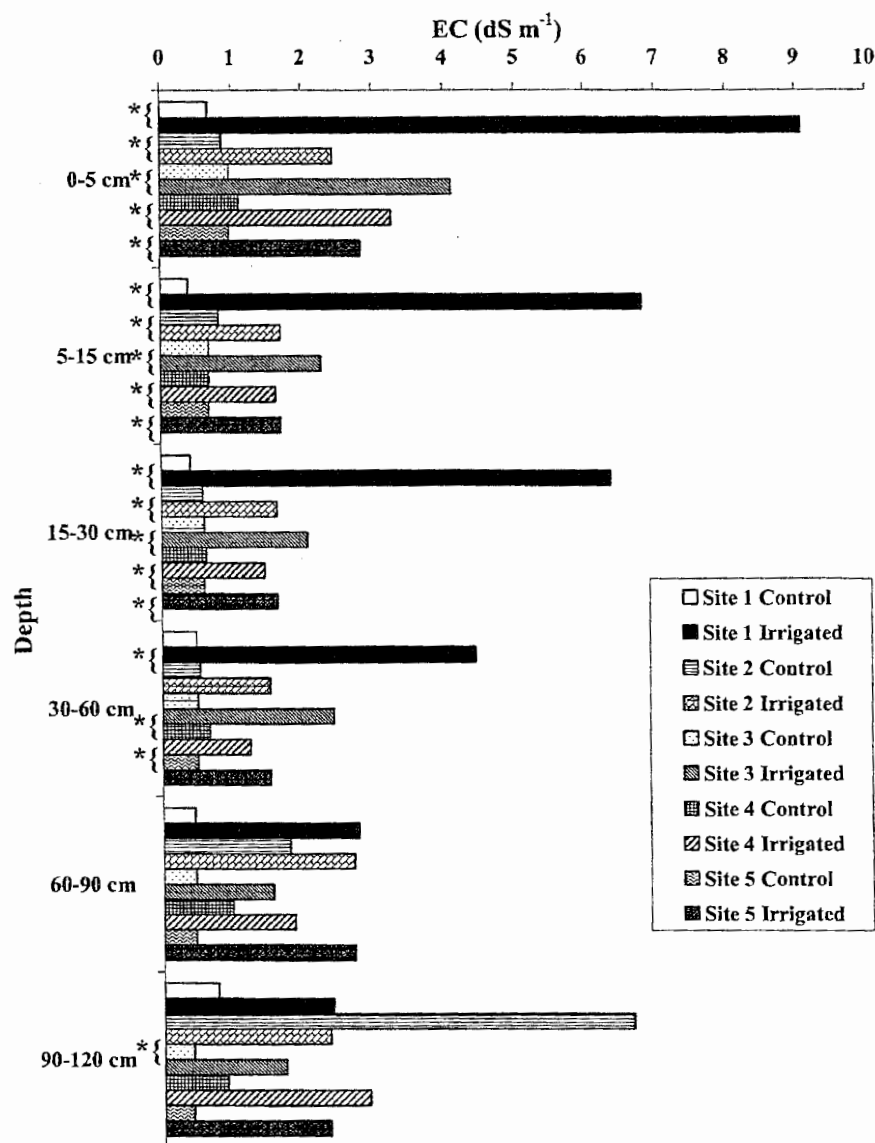
Fig. 3. Mean electrical conductivity of soil saturated paste extracts ($EC_e$) values of soil samples from irrigated and control sites. Significant differences between irrigated and control samples at the 0.05 probability level are noted with asterisks.

trations of Ca and Mg have also increased in all irrigated sites except Site 4, perhaps due to the application of gypsum and possibly CBNG waters, increases in Na concentrations were much greater. As expected, buildup of Na is more pronounced in the fine-textured soils (Sites 1, 3, 4, and 5) than in the loamy soil (Site 2) evaluated in this study (Table 6).

Mass balance calculations (Fig. 5) for Na indicated that both Na addition by CBNG water and mobilization of Na within soil profiles were responsible for Na buildup in these soils. At Site 1, the differences between irrigated and control soil NH₄OAc extractable Na accounted for 73% of Na added by CBNG water. The remaining 27% of Na added by CBNG water could have been lost due to leaching or crop removal. The differences in NH₄OAc

extractable Na between irrigated and control soils at 2, 3, 4, and 5 were 46, 42, 171, and 32%, respectively, more than the Na added from CBNG water, suggesting mobilization of Na in these soils due to salt dissolution from CBNG water irrigation.

An increase in Na concentration in soils causes dispersion of soil clay particles and organic matter, resulting in surface crusting, reduced infiltration, and lower hydraulic conductivity (Park and O'Connor, 1980; Bauder and Brock, 2001). Major clay minerals in soils of the PRB are smectitic clays (Bureau of Land Management, 2003) and these clays exhibit mainly permanent charge (CEC does not depend on pH) because of isomorphic substitution (Frenkel et al., 1978; Igwe, 2001). Thus, dispersion of soils containing smectites is determined mainly by
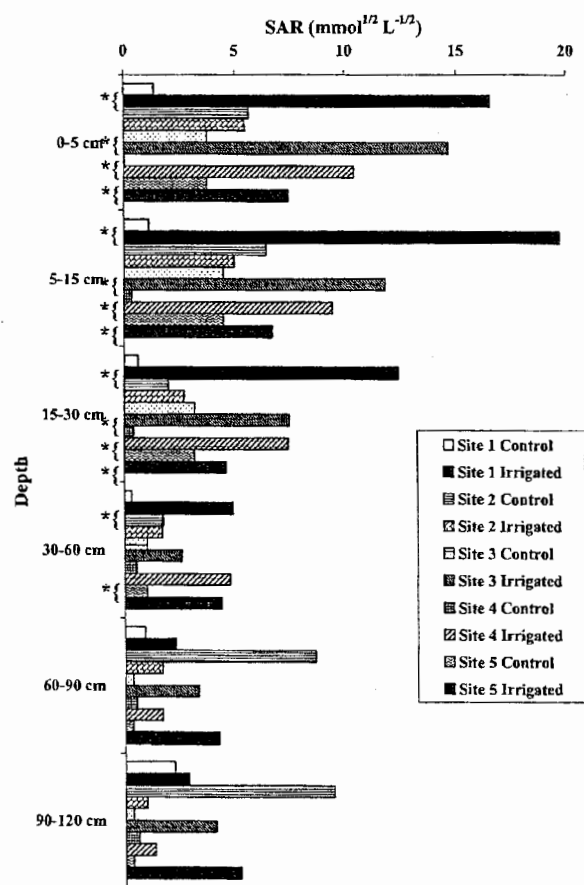
**Fig. 4.** Mean sodium adsorption ratio of soil saturated paste extracts ($SAR_e$) values of irrigated and control sites. Significant differences between irrigated and control samples at the 0.05 probability level are noted with asterisks.

**Table 6. Texture and mean clay contents of soil samples collected from different depths in irrigated and control sites.**

| Depth | Irrigated Texture† | Irrigated Clay | Control Texture† | Control Clay |
|---|---|---|---|---|
| cm | | g kg$^{-1}$ | | g kg$^{-1}$ |
| | | Site 1 | | |
| 0–5 | CL | 370 | CL | 300 |
| 5–15 | C | 490 | C | 410 |
| 15–30 | C | 480 | CL | 360 |
| 30–60 | C | 410 | CL | 350 |
| 60–90 | CL | 370 | CL | 400 |
| 90–120 | CL | 320 | CL | 380 |
| | | Site 2 | | |
| 0–5 | SCL | 200 | SCL | 260 |
| 5–15 | SCL | 280 | CL | 330 |
| 15–30 | SCL | 320 | CL | 320 |
| 30–60 | CL | 310 | CL | 330 |
| 60–90 | SCL | 300 | CL | 290 |
| 90–120 | SCL | 220 | CL | 290 |
| | | Site 3 | | |
| 0–5 | L | 240 | CL | 360 |
| 5–15 | CL | 270 | CL | 400 |
| 15–30 | CL | 350 | C | 480* |
| 30–60 | CL | 380 | C | 510 |
| 60–90 | SCL | 300 | C | 560* |
| 90–120 | SCL | 220 | C | 430* |
| | | Site 4 | | |
| 0–5 | CL | 330 | C | 420 |
| 5–15 | C | 410 | C | 470 |
| 15–30 | C | 420 | C | 440 |
| 30–60 | CL | 390 | CL | 390 |
| 60–90 | CL | 380 | CL | 390 |
| 90–120 | CL | 360 | CL | 360 |
| | | Site 5 | | |
| 0–5 | SCL | 220 | CL | 360 |
| 5–15 | SCL | 320 | CL | 400 |
| 15–30 | C | 500 | C | 480 |
| 30–60 | C | 520 | C | 530 |
| 60–90 | C | 520 | C | 560 |
| 90–120 | C | 560 | C | 430 |

\* Significant differences between irrigated and control samples at the 0.05 probability level.
† C, clay; CL, clay loam; L, loam; SCL, sandy clay loam; SL, sandy loam.

**Table 5. Saturated paste extract Na, Ca, and Mg concentrations in irrigated and control site soil samples.**

| Depth | Irrigated Site 1 | Irrigated Site 2 | Irrigated Site 3 | Irrigated Site 4 | Irrigated Site 5 | Control Site 1 | Control Site 2 | Control Site 3 | Control Site 4 | Control Site 5 |
|---|---|---|---|---|---|---|---|---|---|---|
| cm | | | | | mg L$^{-1}$ | | | | | |
| | | | | | Na | | | | | |
| 0–5 | 1934 | 221 | 763 | 581 | 360 | 56 | 111 | 58 | 35 | 58 |
| 5–15 | 1584 | 108 | 448 | 291 | 181 | 25 | 109 | 51 | 58 | 51 |
| 15–30 | 1285 | 105 | 373 | 233 | 198 | 11 | 57 | 47 | 52 | 47 |
| 30–60 | 554 | 169 | 217 | 180 | 209 | 11 | 22 | 61 | 65 | 61 |
| 60–90 | 208 | 712 | 176 | 94 | 502 | 42 | 94 | 207 | 58 | 207 |
| 90–120 | 201 | 845 | 217 | 107 | 600 | 94 | 495 | 310 | 54 | 310 |
| | | | | | Ca | | | | | |
| 0–5 | 541 | 253 | 274 | 181 | 272 | 60 | 38 | 78 | 186 | 78 |
| 5–15 | 331 | 139 | 84 | 39 | 115 | 35 | 31 | 37 | 80 | 37 |
| 15–30 | 469 | 213 | 113 | 40 | 121 | 44 | 33 | 32 | 62 | 32 |
| 30–60 | 430 | 196 | 258 | 51 | 68 | 46 | 31 | 26 | 62 | 26 |
| 60–90 | 255 | 168 | 110 | 183 | 179 | 24 | 128 | 109 | 58 | 109 |
| 90–120 | 161 | 274 | 106 | 274 | 193 | 28 | 294 | 213 | 53 | 213 |
| | | | | | Mg | | | | | |
| 0–5 | 298 | 13 | 30 | 43 | 12 | 18 | 7 | 10 | 41 | 10 |
| 5–15 | 124 | 27 | 17 | 19 | 26 | 10 | 5 | 4 | 28 | 4 |
| 15–30 | 207 | 50 | 47 | 21 | 40 | 13 | 7 | 6 | 25 | 6 |
| 30–60 | 288 | 70 | 167 | 35 | 72 | 15 | 15 | 9 | 28 | 9 |
| 60–90 | 271 | 155 | 76 | 103 | 423 | 14 | 79 | 83 | 26 | 83 |
| 90–120 | 179 | 235 | 85 | 194 | 415 | 17 | 347 | 188 | 23 | 188 |
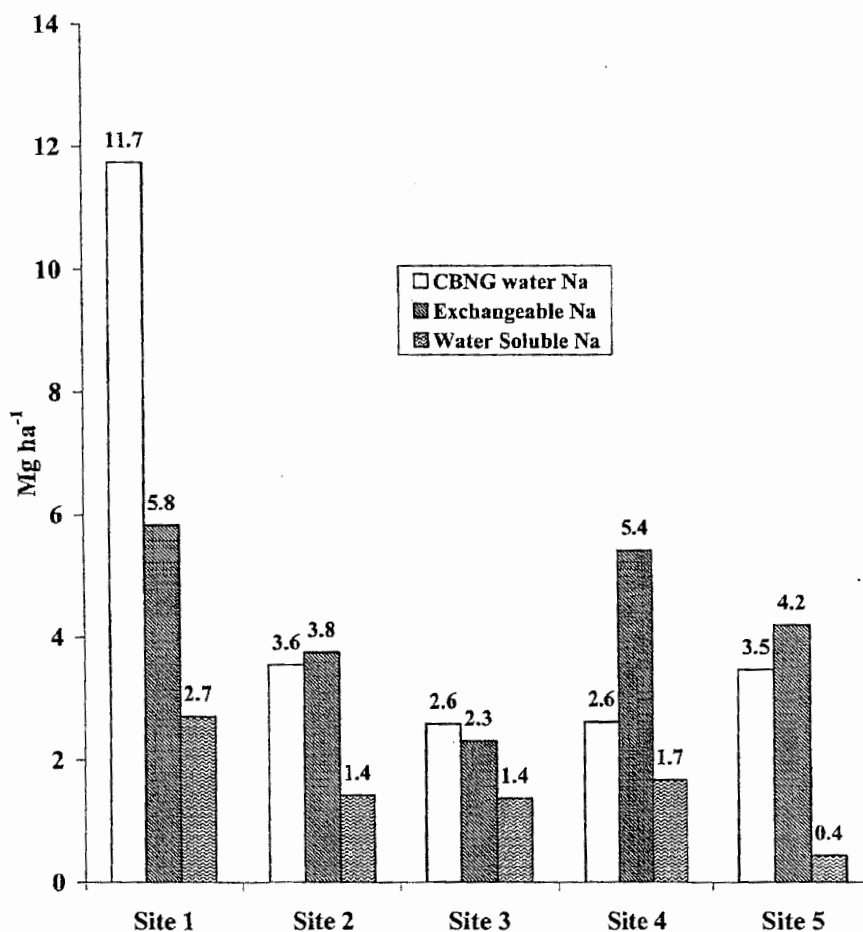
Fig. 5. Cumulative amount of Na added in coalbed natural gas (CBNG) water (over 2 yr in Sites 3 and 4; 3 yr in Sites 1, 2, and 5), and the differences between means of the mass of exchangeable Na and water-soluble Na calculated for the irrigated and control site soils to a depth of 120 cm.

the presence of $Na^+$ on soil exchange sites and soil solution electrolyte concentration (Shainberg et al., 1989). Other related studies at our PRB research sites have found that irrigated soils had lower infiltration rates and Darcy flux rates than did soils at control sites (King et al., 2004). Increased $SAR_e$, Na concentrations, and deterioration of soil physical properties confirmed the sodicity hazards in CBNG irrigated sites.

In an effort to minimize the adverse impacts of direct application of CBNG water to soil, some CBNG producers have adopted water treatment practices such as passing CBNG waters through sulfur burners before land application. Sulfur burners acidify CBNG water with sulfurous ($H_2SO_3$) or sulfuric ($H_2SO_4$) acids, depending on the redox status, to reduce $HCO_3^-$ concentrations. Under acidic conditions $HCO_3^-$ is converted into gaseous $CO_2$ that escapes into the atmosphere. Acidic water also helps solubilize soil minerals such as calcite ($CaCO_3$) and gypsum ($CaSO_4$) (Yu et al., 2003). In our study, we observed that sulfur burners were not in continuous operation throughout the irrigation season. Therefore, inconsistent supply could have contributed to variable

Na concentrations and SAR values in CBNG-water irrigated sites as compared to those of control sites.

Mitigation of sodic conditions requires an increase in $Ca^{2+}$ on the soil exchange complex. The most popular method of increasing $Ca^{2+}$ concentrations in Na-affected soil is through addition of gypsum (Oster, 1982; Shainberg et al., 1989; Bauder and Brock, 2001). In saline soils, gypsum solubility increases due to the presence of soluble salts in the soil solution. Overall, gypsum solubility is also promoted by $Ca^{2+}$ exchange for other cations. Gypsum dissolution rates also depend on physical parameters such as soil water flux and size of gypsum particles, both of which are important parameters affecting the efficiency of gypsum amendments (Kemper et al., 1975). From Table 3, it is evident that gypsum application rates vary among CBNG companies. Based on results of our study, the amount of gypsum applied may not be adequate to counter $Na^+$ added from CBNG water and/or the particle size of the gypsum utilized may not be optimal for enhanced dissolution. Our irrigated sites generally contained greater amounts of Ca and Mg than control sites, which suggest both CBNG waters and gyp-

sum additions contributed to the increased Ca and Mg soil contents. However, Na concentrations in irrigated sites greatly exceeded (especially in Site 1) concentrations of Ca and Mg needed to counter a potential sodicity hazard that could develop on the CBNG irrigated sites. Gypsum amendments may be an acceptable practice for counteracting the high Na concentrations present in CBNG waters, but one must take into consideration the amount of gypsum applied and its particle size, potential for precipitation of Ca as calcite that may result in clogging of soil pores, as well as the lower soil water flux in CBNG irrigated soils influencing gypsum amendment efficiencies. Applications of elemental S to soil can also improve soil $Ca^{2+}$ supply by producing sulfuric acid, which increases dissolution of in situ $CaCO_3$, commonly found in arid and semiarid soils (United States Salinity Laboratory Staff, 1954; Sameni and Kasraian, 2004). However, oxidation of elemental S to sulfite is a slow biological process (Gupta and Abrol, 1990) and production of sulfuric acid from elemental S at our research sites might not have been enough to overcome soil alkalinity.

## CONCLUSIONS

Results of this study suggest CBNG waters used for irrigation in northwestern PRB, Wyoming, are generally unsuitable for direct land application. Soil analyses indicated there were buildups of salt and $Na^+$ in root zones of irrigated sites. Although differences in soil $EC_e$ and $SAR_e$ were more pronounced between irrigated and control soils at Site 1 (site has fine-texture soils and was subjected to longer periods of CBNG water irrigation than the other sites), trends of salt and Na accumulation in other sites were evident. This study demonstrates the potential problems that might arise due to land application of saline-sodic CBNG waters. Therefore, suitable precautionary measures and proper treatment of CBNG water, especially removal of excess Na, are necessary before it should be used for irrigation and/or land disposal. Specific crop and amendment combinations should be developed to improve the efficiency of soil salinity and sodicity management. It is expected that CBNG production will continue to develop at a rapid rate, creating economic benefits and extensive environmental impacts on the PRB environment. Addressing these impacts in a meaningful way will require continued research efforts to understand long-term effects of land application of CBNG waters.

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